ANALYSIS OF OXYGEN IN POTASSIUM

NASA Round-Robin Meeting Held June 4, 1964

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MINUTES OF THE MEETING

(Compiled by Glenn R. Zellars)

A meeting was held on June 4, 1964, at the NASA Lewis Research Center to discuss the results of the NASA sponsored round-robin analysis of oxygen in potassium. The following organizations had participated in the analysis: Dow Chemical Company, Metals Department; General Electric Company, MSD; MSA Research Corporation; NASA Lewis Research Center, Liquid Metals Branch and Chemical Services Unit; Oak Ridge National Laboratory, Analytical Chemistry Division; Pratt & Whitney Aircraft, CANEL; United Kingdom Atomic Energy Authority, Reactor Materials Laboratory; and United Nuclear Corporation, Development Division.

Each participant had been asked to analyze two series of potassium samples for oxygen content: a low and a high series. In addition, each participant was asked to submit a description of his analytical procedure, which is herein collected. For the sake of organization, some liberties have been taken in the chronology of the minutes of this meeting; however, no material pertinent to the proceedings has been consciously omitted.

MORNING SESSION

Dr. Louis Rosenblum of Lewis served as general chairman. In his opening remarks, he stated that much concern had been expressed about the validity of current analytical methods used for the determination of oxygen in potassium. This round-robin analysis is the outgrowth of this concern. It was the hope that this cooperative effort would (1) indicate which method or methods gave the most consistent results, (2) offer a comparison of analytical values derived by different methods, and (3) point to improvements that could be made in current methods.

Mr. Glenn R. Zellars of Lewis described the method of preparation of potassium samples for the round-robin analyses. MSA low-sodium-grade potassium was cold trapped at 160° F for 24 hours and filtered through a 5-millimicron filter, hot-gettered with titanium sponge at 1300° F for about 48 hours, and then vacuum distilled at a pressure of about 10^{-5} torr into a stainless steel container. In a vacuum chamber, the potassium was transferred to stainless steel sample tubes. Figure 1 shows the potassium distributor and the cylindrical can heater used to effect the transfer of the potassium from the collection pot to the tubes. After the potassium had solidified in the tubes, the vacuum chamber was backfilled with argon, and the sample tubes were detached from the
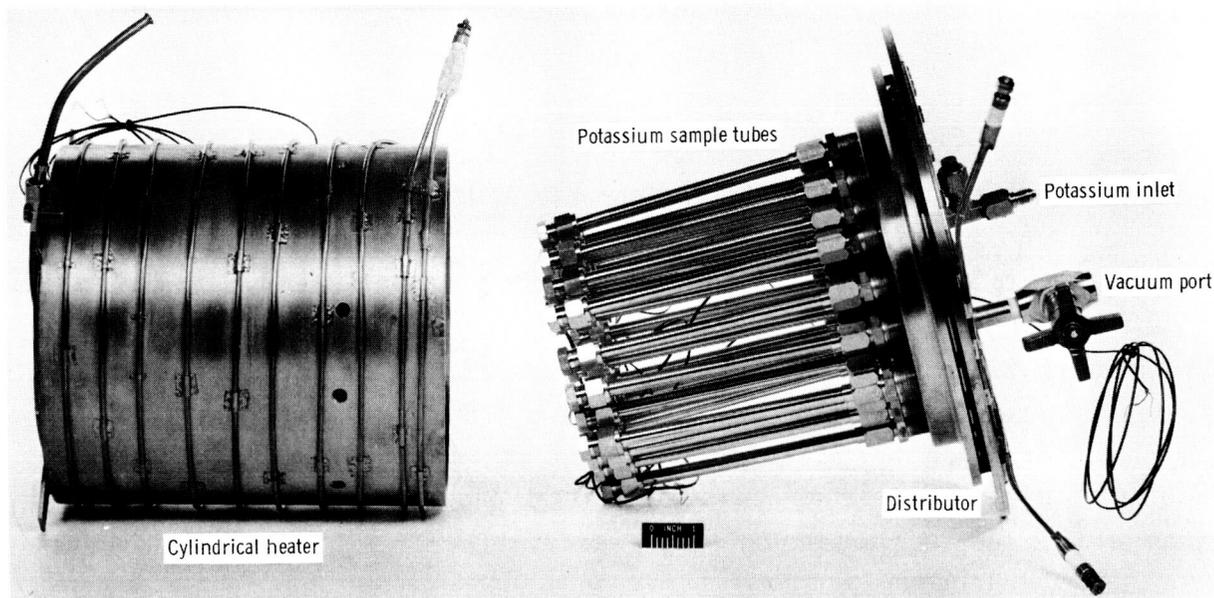
Figure 1. - Potassium distributor and heater apparatus.

distributor, capped, and stored under vacuum for future use. This potassium was designated the "B series" or "Round Robin I."

The "doped" (or higher oxide level) potassium was prepared and handled in the same manner as the B-series except that it was vacuum distilled into a stainless steel container at a pressure of approximately 10^{-3} torr (an adjusted pressure produced by leaking in oxygen gas through a control leak valve). As before, the potassium was transferred from the collection pot to stainless steel sample tubes. These tubes were labeled the "E series" or "Round Robin II."

A question was asked as to the order in which the tubes were detached from the distributor and the possible degree of homogeneity. In answer to the question, Mr. Zellars stated that it is believed that the tubes were filled at random from the inlet of the distributor, but that the tubes were detached in a particular order and so numbered. The analytical data, obtained by NASA before samples were sent to the various analysts, indicated that the potassium was uniform within as well as between sample tubes. Further, the data suggested that no trend of oxygen content in the potassium occurred with tube position on the distributor.

The next speaker, Mr. Randall F. Gahn of Lewis, described the vacuum distillation apparatus used at Lewis. He explained that although most of the analysis at Lewis was performed by the mercury amalgamation method, checking results against another method was considered advisable.

The potassium samples were extruded to size, cut, and dropped into the reaction crucible by means of a vacuum extrusion technique. The crucible was inductively heated

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to about 300° C for a period of 6 to 8 hours to distill the potassium. After the distillation was completed, the apparatus was backfilled with dry argon. The crucible was removed and rinsed with carbon dioxide free water, and the solution was titrated with standard acid to phenolpthalein and methyl red end points. Good agreement was obtained between the vacuum distillation method and the mercury amalgamation for low values of oxygen in potassium, approximately 50 ppm or less.

Mr. Gahn reported that the sample size was normally 1 to 2 grams, and probably the distillation was completed within 2 to 3 hours, but that he generally heated the samples for 6 to 8 hours to ensure complete removal of the potassium. He stated that potassium with "high" oxygen levels exhibited a reaction between the "oxide" and the glass crucible. Nickel crucibles showed a similar effect. No evidence of any reaction was noticeable when the oxygen content of the potassium was "low."

Mr. George Cobel of Dow Chemical Company asked whether an attempt had been made to identify the species from either the mercury amalgamation or the vacuum distillation techniques. Mr. Gerald Goldberg of Oak Ridge National Laboratory said that this has been tried, but no one has been successful because of great difficulty in collecting and transferring the residues for analysis.

Dr. Rosenblum opened the discussion of the overall results of Round Robins I and II. Figure 2 shows the position of each tube of potassium on the distributor, the tube that each cooperator received, the oxygen analyses each reported and the various methods used.

Table I is a brief statistical presentation of the data for Round Robin I. Averages of the results from each participant are presented as well as the respective standard deviations. The following results were discarded:

(1) Results from P&W obtained by the ammonia method. Mr. E. W. Hobart of the company stated that the analyses by this method were unreliable.

(2) The value of 183 ppm for tube B-17. Mr. C. C. Gregg of United Nuclear said that a poor atmosphere developed in the dry box during the cutting of the sample.

From table I, several observations can be made about the results:

(1) Agreement was found among the analyses by NASA, MSA, and ORNL.

(2) From the values obtained by NASA, MSA, and ORNL for standard deviation in the case of single-tube analyses and also from the overall standard deviations among the several tubes (randomly selected), it is possible to conclude that the samples exhibited homogeneity within tubes and did not vary appreciably between tubes.

(3) Higher values and higher standard deviations within and between tubes were obtained by the other participants.

For the second round robin, NASA attempted to "spike" the potassium to an oxygen level of about 100 ppm. The analyses from tubes E-2, E-12, and E-22 indicated that the potassium contained about 117 ppm oxygen, and the samples appeared to be homogeneous.

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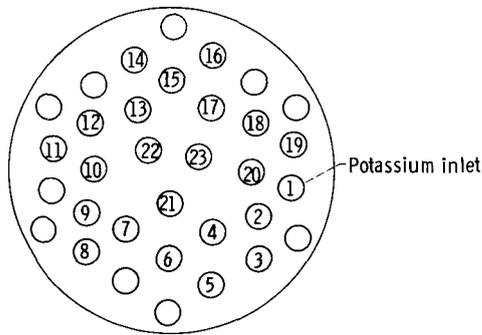
Position of tubes on distributor
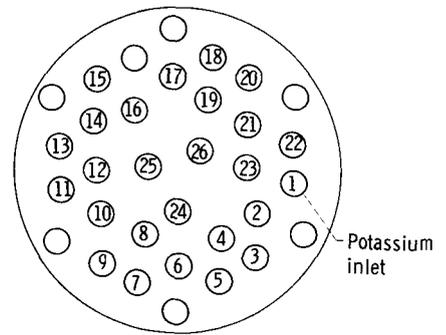
Position of tubes on distributor

Tube	Participant	Oxygen, ppm	Method of analysis
1	----------	----------------	----------------
2	Dow	----------------	----------------
3	NASA	23.3, 19.5	Hg amalgamation
4	NASA	29.1, 29.8, 28.6	Hg amalgamation
5	United Nuclear	46, 50, 39	Hg amalgamation
6	United Nuclear	49, 40, 66	Hg amalgamation
7	NASA	40, 50	Vacuum distillation
8	Pratt & Whitney	49 / 49	Hg amalgamation / Ammonia
9	NASA	----------------	----------------
10	UKAEA	105, 125	Vacuum distillation
11	Dow	----------------	----------------
12	NASA	25.8, 26.5, 27.7	Hg amalgamation
13	Pratt & Whitney	117, 131 / 47	Hg amalgamation / Ammonia
14	UKAEA	105, 140	Vacuum distillation
15	MSA	17, 22, 25	Hg amalgamation
16	ORNL	22, 26, 24	Hg amalgamation
17	United Nuclear	183, 40, 40, 32	Hg amalgamation
18	MSA	28, 27, 30	Hg amalgamation
19	Pratt & Whitney	117, 143, 49	Hg amalgamation
20	ORNL	21, 19, 22	Hg amalgamation
21	General Electric	84.5, 90.0, 83.5	Hg amalgamation
22	General Electric	79.9, 77.6, 103.0	Hg amalgamation
23	General Electric	19.2, 102.8, 105.3, 84.1	Hg amalgamation

(a) Round Robin I (series B).

Tube	Participant	Oxygen, ppm	Method of analysis
1	NASA	----------------	----------------
2	NASA	101 / 500	Hg amalgamation / Vacuum distillation
3	ORNL	88, 92, 91	Hg amalgamation
4	NASA	----------------	----------------
5	NASA	----------------	----------------
6	NASA	----------------	----------------
7	NASA	----------------	----------------
8	NASA	----------------	----------------
9	NASA	----------------	----------------
10	Pratt & Whitney	296, 442, 533	Hg amalgamation
11	NASA	1090, 1220. 985, 1120, 535, 625	Vacuum distillation
12	NASA	118, 115, 116	Hg amalgamation
13	NASA	----------------	----------------
14	ORNL	90, 85, 84	Hg amalgamation
15	NASA	----------------	----------------
16	Pratt & Whitney	394, 271 / 43, 18	Hg amalgamation / Ammonia
17	NASA	----------------	----------------
18	NASA	----------------	----------------
19	NASA	----------------	----------------
20	NASA	----------------	----------------
21	NASA Chemical Services	1093, 1073, 1120	Hg amalgamation
22	NASA	119, 114, 118	Hg amalgamation
23	Pratt & Whitney	----------------	----------------
24	General Electric	316, 466, 387	Hg amalgamation
25	General Electric	317, 466, 705	Hg amalgamation
26	General Electric	738, 939, 742, 466	Hg amalgamation

(b) Round Robin II (series E).

Figure 2. - Results of analysis of oxygen in potassium in relation to position of tube on distributor.

From the handling technique and from the analysis, series E seemed quite satisfactory. Samples were then sent out to the cooperators. The results of Round Robin II are shown in figure 2(b) and table I.

The first hint that all was not well came when the results on tube E-21 were returned from the Lewis Chemical Services Unit. This group had analyzed other potassium samples for oxygen and its results had generally agreed with those of the Liquid Metals Branch. When the former group gave an average value of 1095 ppm oxygen for tube E-21, there was cause for concern. Further, the subsequent use of the vacuum
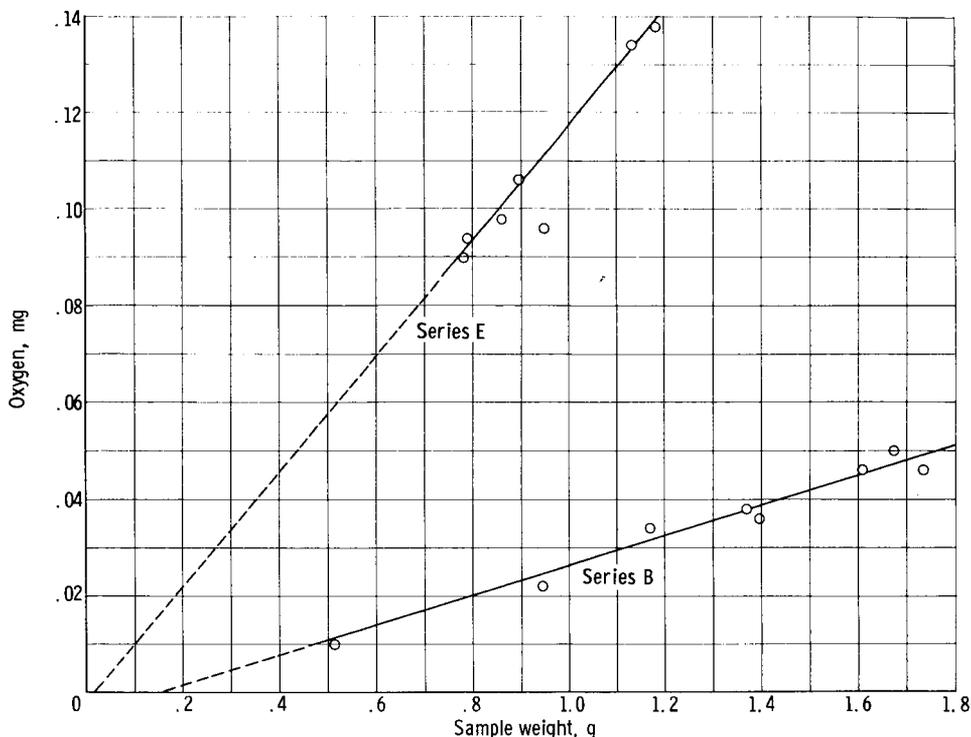
Figure 3. - Estimation of oxygen blank from NASA data.

distillation method (glass crucibles) on tube E-11 indicated that this potassium had an oxygen content of about 1100 ppm. (Lower values of 525 and 625 on tube E-11 and the value of 500 on tube E-2 were obtained with a nickel crucible.) These data are shown in table II and figure 2(b).

The large discrepancy among these analyses led to an investigation of the applicability and the limitations of the mercury amalgamation method to the "doped" potassium. It was observed that if the potassium and mercury were allowed to react rapidly, generating much heat, low values for the amount of oxygen resulted. On the other hand, if the potassium was reacted very slowly with the mercury without an appreciable rise in temperature, higher oxygen values were obtained. This "hot or cold effect" was found only with those potassium samples in which the oxygen level had been increased by intentionally "spiking" with oxygen gas. Untreated potassium samples, nominally below 100 ppm oxygen, have not shown this temperature effect.

There was considerable discussion about the causes of the great spread of oxygen values in the second round robin. The points discussed included the purity of the oxygen gas used, the homogeneity of the samples, solubility of the "oxide," particle size, "oxide" species, and others. No conclusions were reached.

Round Robin II results can be summarized as follows:

(1) There is general agreement between the "hot" amalgamation results from ORNL and NASA, approximately 100 ppm oxygen.

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(2) Results of vacuum distillation (in glass crucibles) and "cold" mercury amalgamation agree well; they give an alkalinity equivalent to about 1100 ppm oxygen in the potassium samples.

(3) General Electric and Pratt & Whitney results fall near the middle of the extremes - between 100 and 1000 ppm oxygen.

To ascertain the size of a blank that may be inherent in the vacuum mercury amalgamation method, NASA varied the weight of the samples of potassium from about 1/2 to nearly 2 grams. A plot of the sample weight against the milligrams of oxygen is shown in figure 3 for Round Robins I (series B) and II (series E). Extrapolation of the curves to zero sample weight leads to practically a zero blank.

AFTERNOON SESSION

Mr. Cobel gave a report on the technique for the determination of the oxygen content in cesium by neutron-activation analysis. He said a special plastic containment material for vials (with very low oxygen content) had to be made before any degree of success was obtained. Activation analysis could possibly develop into a referee method for oxygen analysis in alkali metals (ref. 1).

At the conclusion of the report by Mr. Cobel, Dr. Rosenblum invited comments from the participants on the round-robin analysis. Mr. Cobel stated that the alkyl halide method for determining oxygen in potassium was unsuccessful because removal of all traces of water from the reagents was practically impossible. In addition, the formation of an ether instead of the alcoholate caused large inaccuracies.

Mr. E. W. Hobart of Pratt & Whitney said that the ammonia method for the analysis of oxygen in potassium was unsatisfactory. He talked further about the assumptions made in applying the mercury amalgamation method to the analysis of oxygen in potassium, quoting from reference 2.

Dr. Wilson Mausteller of MSA Research Corporation injected a practical observation that summed up the view of all the participants. "We cannot stop our alkali metal testing just because our yardstick is 6 feet long. We must do the testing while continuing to look for the proper analytical tools."

Despite the problems and uncertainties brought out in the first two round robins, all felt that another round robin was warranted and agreed to participate. Several recommendations and suggestions were made:

(1) If possible, samples should be contained in 1/2-inch-diameter tubes.

(2) Cooperators should vary the weight of potassium samples so that their blanks may be established.

(3) Oxide species, for example, K_2O, K_2O_2, K_2CO_3, should be identified if possible.

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Mr. A. P. Litman from ORNL volunteered to prepare some K_2O doped potassium for distribution.

The chairman, Dr. Louis Rosenblum, thanked all persons for their attendance and participation in this round-robin analysis.

REFERENCES

1. Stenger, V. A., et al.: Analytical Methods for Impurities in Cesium Metal. Rept. No. ML-TDR-64-199, Final Rept. July 1, 1963-May 25, 1964, Dow Chem. Co., Aug. 1964.

2. Hobart, Everett W., Jr.: Remarks on the Analysis of Alkali Metals. CNLM-5676, Paper Presented to AEC Sodium Components Dev. Group, Alkali Metal Analysis Symposium, Hollywood (Calif.), Apr. 14, 1964.

TABLE I. - STATISTICAL ANALYSIS OF ROUND ROBINS I AND II (SERIES B AND E)

Laboratory	Method	Oxygen, ppm			
		Overall		Individual tube	
		Average	Standard deviation	Average	Standard deviation
Series B					
United Nuclear	Hg amalgamation	44.3	10	44, 52, 37	7.2, 15.7, 4.6
Oak Ridge	Hg amalgamation (flame for K)	22.3	2.4	24, 21	2.0, 1.53
MSA	Hg amalgamation	25	4.7	21, 28	4.0, 1.36
U.K.A.E.A.	Vacuum distillation: Photometric, titration	120 / 124	11.5 / 17	----- / -----	-------- / --------
General Electric	Hg amalgamation Flame for K	90.1 / 88.0	10.8 / 14.9	86, 97 / 80, 104	9.2, 11.6 / 8.0, 12.7
NASA	Hg amalgamation (vacuum)	26.3	3.7	27, 29, 21.4	1.0, 0.6, 2.7
Pratt & Whitney	Hg amalgamation	101.0	41.4	49, 124, 103	0, 9.8, 48.0
Series E					
General Electric	Hg amalgamation Flame for K	554 / 589	212 / 208	721, 496, 390 / 779, 502, 424	194, 196, 75 / 177, 137, 64
NASA	Hg amalgamation	116.8	2.01	116.6, 117.0	1.55, 2.74
Oak Ridge	Hg amalgamation (flame for K)	86.3	3.3	90.3, 86.3	2.1, 2.1
Pratt & Whitney	Hg amalgamation	387	118	424, 333	119, 87

TABLE II. - SUPPLEMENTARY NASA TESTS OF ROUND ROBIN II (SERIES E)

Laboratory	Method	Tube	Oxygen, ppm		
			Overall	Average	Standard deviation
NASA Chemical Services	Hg amalgamation	E-21	1093, 1073, 1120	1095	23.5
NASA Liquid Metals Branch	Vacuum distillation	E-11, E-2	1090, 1220, 985, 1120 (Glass crucible)	1104	91.0
			535, 625, 500 (Nickel crucible)	553	67.0

UNITED KINGDOM ATOMIC ENERGY AUTHORITY

The potassium was sampled from the tube by melting in an oxygen-free argon atmosphere into hydrogen-fired nickel crucibles. Potassium was removed by vacuum distillation, and the oxide residue titrated with standard sulfuric acid.

PROCEDURE

The sample tubes were loaded into a dry box together with a sample of sodium of known oxygen content contained in nickel crucibles of 7-milliliter capacity each with a surface area (i.e., exposed sodium) of 3 square centimeters. The two crucibles containing sodium were contained in a distillation pot sealed under an atmosphere of argon ($<$ 1 vpm oxygen). A further distillation pot under a vacuum of $<$0.1 micron containing hydrogen-fired nickel crucibles was also loaded. A standard 200-watt tubular heater was used to melt the potassium from the tube; this was loaded into the box together with other ancillary handling equipment.

The whole system was evacuated to a vacuum of $<$ 0.1 micron and maintained at this for 12 hours to ensure complete outgassing of equipment. The tubular heater was run up to temperature during this period and maintained at a higher temperature than that used to melt the potassium.

After approximately 12 hours, the dry box was brought up to atmospheric pressure using purified argon ($<$ 1 vpm oxygen). The sodium of known oxygen content was exposed to the dry box atmosphere. Potassium was melted from the bottom and top of the tube into the two hydrogen-fired nickel crucibles. Some difficulty was experienced at this stage in removing the molten potassium from the tube.

After allowing the potassium to solidify, the two crucibles were placed in a nickel carrying tray (designed to give good thermal contact between crucible and base of pot) and placed in a distillation pot. A lid incorporating the extraction valve and cold finger was then bolted down onto the pot with a neoprene O-ring to give a vacuum-tight seal at this point. The two sodium samples were treated in a similar manner in a separate distillation pot.

The whole process from letting the box up to atmospheric pressure to bolting down the sodium distillation pot lasted approximately 30 minutes.

The distillation pot was attached to a unit consisting of a vacuum line and heating facilities and was evacuated via the extraction valve down to a vacuum of 0.1 micron;

the cold finger was filled with water and kept cool by means of a continuous flow of water. Heat was then applied to the pot.

The distillation was carried out under continuous vacuum for 6 hours at 350° C. At the end of this period, the pot was allowed to cool to room temperature still under vacuum. It was then removed from the distillation unit and brought up to atmospheric pressure by bleeding air in slowly via the extraction valve.

After removal of the cold finger containing potassium from the pot, the carrier holding the two crucibles was removed. A solution of bromocresol purple (0.001 percent solution) was prepared using carbon dioxide free water, and the residue of potassium oxide was washed from the crucible. The resultant alkaline solution was titrated with 0.01 N sulfuric acid solution.

Following the titration, the solutions were diluted to known volumes and the potassium and sodium determined by a flame photometer equipped with a cool gas-air burner and a variable light filter system.

RESULTS

Sample	Tube area	Oxygen, ppm		
		Titration	Photometric	
			As potassium	As sodium
B10	Bottom	110	105	5
	Top	130	125	5
B14	Bottom	110	105	5
	Top	130	140	5

Sodium Control

Direct determination, ppm 10
Glove box sample, ppm 10

ACCURACY

The sample available from each tube was restricted and below the normal amount, which entailed an approximation when determining weight taken for each crucible. Our experience indicates that the accuracy of the above figures is within ±10 percent of the true value.

PRATT & WHITNEY AIRCRAFT

CANEL MATERIALS LABORATORY MANUAL

ANALYTICAL SECTION

Principle. - When sodium, potassium, or NaK are amalgamated with mercury under an inert atmosphere, their oxides, being insoluble in the mercury, separate from the amalgam and rise to the surface. Repeated separations and additions of mercury serve to isolate the alkali metal oxides from the alkali metal. They are then dissolved in water and titrated.

Scope. - The procedure may be used for the determination of oxygen in alkali metals in the range of 0.001 to 1 percent.

Apparatus. - Inert atmosphere dry box, 250-milliliter Pyrex separatory funnels.

Precautions. - As the alkali metals are very reactive, the samples must be protected from atmospheric contamination at all times. The amalgamation reaction of mercury with the alkali metals produces considerable heat which must be dissipated successfully. It is necessary to guard against spillage and fire accidents when handling alkali metal samples or residues. Safety goggles must be worn during operations involving these metals.

Reagents. -

   Sulfuric acid, 0.5 N - Prepared and standardized

   Sulfuric acid, 0.002 N - Prepared by diluting 8 milliliters of 0.5 N sulfuric
      acid to 2 liters. Standardized

   Sodium hydroxide, 0.5 N - Prepared and standardized

   Mercury, triple distilled

Procedure. - The following operations are performed in an inert-atmosphere dry box:

Add approximately 20 milliliters of mercury to a 250-milliliter Pyrex separatory funnel. To this add 0.5 to 1 gram of the alkali metal sample. Shake for about 3 minutes, hold for 30 seconds, and draw off all but 3 milliliters of the amalgam into a marked beaker. (Current practice is to weigh samples to ±0.01 gram using "Centogram" balance in the dry box at this point.)

Repeat addition and separation of the mercury eight times.

In the last extraction, pour a small portion into a separate beaker to check the completeness of the extraction. (Add water and phenolphthalein to the beaker outside the dry box.)

Remove all the material from the dry box.

Dissolve the oxide from the mercury oxide extract in about 50 milliliters of freshly deionized water and titrate with 2.0×10^{-3} N H_2SO_4 to a bromocresol purple end point (blue to green to yellow).

<u>Calculations.</u> -

$$\text{Oxygen} = \frac{N_a V_a \; 0.008 \times 10^6}{W}, \; \text{ppm}$$

where

N_a	normality of dilute sulfuric acid used to titrate the oxides
V_a	volume of dilute sulfuric acid used
0.008	milliequivalent weight of oxygen
W	weight of sample, g

GENERAL ELECTRIC COMPANY

The amalgamation method for determining the amount of oxygen in potassium was employed to analyze NASA round-robin potassium samples B-21 to B-23. The following report presents the results obtained, the factors considered for assuring the reliability of the results, and a detailed description of the analytical method used.

APPROACH

To obtain the most reliable results from the round-robin samples, the following approach was used:

(1) The argon cover gas was analyzed for oxygen and water content, and the contaminating effects of the entire analytical system were determined on a high-purity potassium sample just prior to analysis of the round-robin samples.

(2) The round-robin samples were then analyzed by the same methods and under the same conditions used in establishing the contaminating effects of the analytical system.

(3) Following the round-robin analyses, the analytical system was again checked for contaminating effects on another high-purity potassium sample from the same batch as before to determine whether any changes in system reliability had occurred.

ARGON COVER GAS ANALYSIS

The argon cover gas used in the amalgamation method as employed here is considered the most significant source of any oxygen and/or water contamination which occurs during an analysis. Thus, determination of these contaminants was necessary.

The oxygen content of the argon was measured by the Brady method. This technique involved passing the argon through an aqueous solution of sodium anthraquinone beta sulfonate, which dissolves the oxygen and is decolorized by oxidation of the reagent. The change in absorption is determined with a Bausch and Lomb Spectronic-20 spectrophotometer. The apparatus is calibrated with pure argon spiked with oxygen by electrolytic decomposition of aqueous sulfuric acid. The detection limit for our particular setup is 1 microgram of oxygen, and the precision in the range used (10 to 30 μg) is $\pm$1 microgram.

The argon was first passed through the purification train and into the reaction system, following the same path used for an analysis. The effluent gas was then passed through the calibrated Brady apparatus where the transmission of the oxygen sensitive solution was measured against time. The argon flow rate was measured with a wet test meter placed downstream from the Brady apparatus. Two successive determinations indicated 0.28 ± 0.03 and 0.16 ± 0.03 vpm oxygen in the argon.

The argon dewpoint was measured using an Electrodryer polished mirror cap. The mirror was slowly cooled by adding dry ice to acetone. The argon impinged on the cool mirror surface at a rate of 5 standard cubic feet per hour after passing through the reaction system. The temperature at which the first sign of frost appeared on the mirror was considered the dewpoint. Successive determinations produced dewpoints at about -101° F.

The combined volume of the sample cutting and reaction sections of the amalgamation apparatus is about 40 cubic inches. Thus it was calculated that the system full of argon at 17 pounds per square inch absolute would contain about 0.25 microgram of oxygen and 1.0 microgram of water. Since the potassium and amalgam are exposed to four argon fills during analysis, the estimated contamination by argon was 6 micrograms of oxygen or less.

CONTAMINATING EFFECTS OF SYSTEM

In addition to the argon, other possible sources of contamination are adsorbed gases on flask surfaces and cutter wires, impurities in the mercury, and leakage of air into the system under both vacuum and positive argon pressure. Since it is not possible to measure the separate effects of these contamination sources, a total system blank was determined.

Assuming the contamination sources to be relatively constant, a series of analyses was performed using different sample weights of hot trapped potassium, which was known from previous experience to yield low oxygen values. The sample was taken into an evacuated tube in essentially the same way the round-robin samples were obtained.

Examination of the X-ray photographs prior to analysis indicated that both B-21 and B-23 had voids which extended about two-thirds of the length. The B-22 sample tube appeared full, but the potassium was seamed and cracked in the bottom fourth of the tube. Therefore, it was decided to analyze B-21 and B-23 first to determine whether reproducible results could be obtained from them.

The B-21 mailing tube was cut open in air with a hacksaw. When the tube was penetrated, there was no audible hissing of air into the tube to indicate a reduced pressure inside. The tube was cut and flared at the point shown on the X-ray photograph. The

expected void was there but was sealed off quickly during the removal of about 1/2 inch of potassium in preparation for flaring the tube. During the process of extruding sections from B-21, the presence of the void caused the potassium to issue forth from the tube after intentional extrusion had stopped. The comments concerning the samples obtained from B-21 are recorded in table III. The expected void was found in 62B. The titration values were reasonably precise, as shown in tables I and II, while the flame values showed a high blank and were considerably less precise. The reasons for the differences are not known, although the presence of halogen compounds or oxides of other metals could produce "oxide" values for titration which differ from flame photometric values if operator or instrument errors may be excluded.

The B-23 mailing tube was under a slight vacuum when opened. The behavior and appearance of the samples from B-21 and B-23 were quite similar. The first two samples from B-23 had oxygen values nearly equal by both titration and flame. The third sample was about 25 ppm higher by flame in oxygen content than the first two. The blank was calculated on the titration results. The third sample from B-23, that is, 63C, was taken from a section which could have been contaminated because of the void, as shown on the X-ray photograph.

The results on B-21 and B-23 were fairly consistent, although about 50 ppm higher in oxygen content than expected. However, the presence of voids in these samples indicated that some contamination probably had occurred. It was expected that sample B-22, having no long longitudinal voids, would produce oxygen values at the indicated 35 ppm level.

The B-22 mailing tube was also under a slight vacuum. There were no voids and all samples appeared to be of good quality. The first sample from B-22, that is, 64A, had 19.2 ppm oxygen by titration. The next three samples, however, were essentially at the oxygen level found in B-21 and B-23. Again no blank was determined.

To determine whether the high values obtained from the round-robin samples were caused by some change in the cover gas, mercury, etc., another sample of the hot trapped potassium was analyzed after B-22. The results shown for sample 65 are almost identical to those obtained on sample 61, which was analyzed before B-21.

It must be emphasized that the 17 analyses shown in table I were performed in, as nearly as possible, the same way. Therefore, it must be concluded that the round-robin samples B-21 to B-23 had oxygen contents 50 to 70 ppm higher than the hot trapped potassium used for the system checkout.

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TABLE I. - ROUND-ROBIN ANALYTICAL RESULTS

Sample identity	Sample	Sample weight, g	Flame					Titration	
			Residue volume, ml	Oxygen as K_2O, μg	Oxygen as Na_2O, μg	Total oxygen, μg	Total oxygen, ppm	Total oxygen, μg	Total oxygen, ppm
6/27/64; lined 5-lb hot trap	61A	1.228	48.9	30.6	3.7	34.3	27.9	26.6	21.6
	B	.786	48.9	8.5	1.5	10.0	12.7	12.1	15.8
	C	.970	48.2	12.6	2.9	13.5	16.0	11.4	11.8
	D	1.650	49.1	20.9	2.3	23.2	14.1	17.8	10.8
7/1/63; B-21	62A	1.685	48.5	129.0	11.1	140.1	83.1	142.4	84.5
	B	1.314	47.8	97.0	5.8	102.8	78.1	118.2	90.0
	C	1.103	48.4	99.1	6.7	105.8	93.7	92.1	83.5
7/2/63; B-23	63A	1.642	47.9	110.0	10.9	120.9	73.5	131.3	79.9
	B	1.284	48.9	80.1	11.2	91.3	71.1	99.6	77.6
	C	1.110	48.4	79.3	10.3	89.6	80.7	114.3	103.0
7/3/63; B-22	64Å	1.634	48.7	36.8	3.7	40.5	24.8	31.4	19.2
	B	1.361	48.3	135.4	8.1	143.5	105.4	140.0	102.8
	C	1.103	48.9	119.0	8.9	127.9	115.8	116.3	105.3
	D	1.630	48.4	138.8	8.8	147.6	90.5	137.0	84.1
7/5/63; lined 5-lb hot trap	65A	1.623	48.8	19.4	2.2	21.6	13.3	15.4	9.5
	B	1.384	48.4	15.3	2.8	18.1	13.1	13.4	9.7
	C	1.099	48.7	13.6	3.0	16.6	15.1	13.0	11.8

TABLE II. - ROUND-ROBIN ANALYSES - BLANK DETERMINATIONS

Sample identity	Samples used	Method of analysis	Oxygen, ppm	Oxygen in blank, μg	3σ, μg
Lined 5-lb hot trap	61B, C, D	Titration	7.4	5.4	2.5
		Flame	14.2	.2	3.6
B-21	62A, B, C	Titration	84.0	2.7	11.0
		Flame	63.7	29.2	21.6
B-23	63A, B, C	Flame	62.4	16.7	11.6
Lined 5-lb hot trap	65A, B, C	Titration	4.5	7.8	1.3
		Flame	9.6	5.7	1.6

TABLE III. - ROUND-ROBIN MISCELLANEOUS DATA

[Time under vacuum, 8 to 10 min.]

Sample identity	Sample	Flask	Flask volume, cu in.	Flask leak rate, μ/min	Reaction mixture separation time, min	Separation time between washes, min	Remarks
Lined 5-lb hot trap	61A	1	17.2	0.27	27	3	------------------
	B	P-6	19.3	2.5	13	2-3	Looked dirty after amalgamation.
	C	28780	19.7	3.0	20	3-4	Sample tube sat overnight. Large void in center.
	D	26523	19.3	.55	64	4-5	Large void in sample.
B-21	62A	180	14.3	0.37	115	3-9	Small indentations in sample.
	B	28734	15.0	.78	72	4-9	Reacted upon contact. Void in sample end mushroomed.
	C	28780	19.7	Negligible	123	3-11	------------------
B-23	63A	P-6	19.3	Negligible	110	3-41	Small void in middle of sample.
	B	1	17.2	0.56	131	4-6	Large void in center of sample.
	C	180	14.3	.69	69	5-6	------------------
B-22	64A	P-6	19.3	0.67	100	3-4	Reacted upon contact.
	B	28734	15.0	.73	72	3-19	Looked good.
	C	26523	19.3	.80	80	3-10	Spots on flask insoluble in water.
	D	28780	19.7	.62	5	3-4	------------------
Lined 5-lb hot trap	65A	26523	19.3	0.61	96	3-7	May be contaminated.
	B	P-6	19.3	.87	83	3-10	Reacted upon contact.
	C	1	17.2	.56	95	3	Reacted upon contact.

MSA RESEARCH CORPORATION

by S. J. Rodgers

SAMPLING PROCEDURE

The standard sampling procedure used at MSA Research Corporation is a dip sampling method. Access to the system being sampled is through a $1\frac{1}{2}$-inch ball or gate valve. A sampling apparatus with provisions for inert gas and vacuum is positioned on the valve. After appropriate degassing and purging of the sampling apparatus, the valve is opened and a nickel bucket of approximately 1-gram capacity is lowered into the system. The sample is extracted and transferred under inert gas to an amalgamation chamber. Alkali metal is extracted with mercury according to the standard amalgamation method.

The NASA round-robin samples were received in 3/8-inch stainless-steel tubing; hence, the MSAR standard sampling procedure could not be used. An extrusion device was fabricated to extract potassium samples from the tubing. In practice, the device is evacuated and purged four times and finally filled with inert gas to a pressure of 2 to 3 pounds per square inch gage. Potassium is then extruded and the contaminated end is cut off and discarded. The sample is transferred directly from the extrusion device to an amalgamation chamber.

ANALYTICAL PROCEDURE

The standard amalgamation method is used for analysis of oxygen at MSAR. In general, six mercury extractions are sufficient to remove all the alkali metal, but the mercury effluent is checked with phenolphthalein to establish when all of the metal has been extracted. The residue remaining after extraction is dissolved in distilled, degassed water and the solution is titrated with 0.01 N hydrochloric acid. The end point is determined potentiometrically. The volume of acid required for neutralization is used to calculate the impurity level as oxygen.

Two 3/8-inch-diameter tubes filled with potassium were received from NASA and analyzed for oxygen. The results of these samples were as follows:

Tube	Sample	Oxygen content, ppm
B-15	1	17
	2	22
	3	25
B-18	1	28
	2	27
	3	30

Based on dip samples taken from numerous potassium shipping containers, the reproducibility of results is better than ± 5 ppm of oxygen.

OAK RIDGE NATIONAL LABORATORY

The analysis for oxygen was carried out using a modification of the amalgamation technique as described in reference 1, which also contains a photograph of the apparatus. A complete description of the method will be published at a later date. The stainless-steel tube which contained the potassium was removed from the copper mailing tube just prior to analysis. This tube and three reaction vessels were placed in a high-vacuum dry box (the reaction vessel has been modified in that an O-ring sealed cap was used at the top rather than the transfer stopcock which is pictured in the report). Three sections, each approximately $1\frac{3}{8}$ inches in length, were cut from the tube, and each section, including the stainless-steel tubing, was placed in a separate reaction vessel. These sections were labeled top, middle, and bottom.

The amalgamation was carried out in vacuo at a pressure of approximately 10^{-4} torr. (The mercury used is processed with a Bethlehem Oxified Unit.) The residue which remained after amalgamation was dissolved in approximately 0.02 N hydrochloric acid; the solution was diluted to volume, and the potassium was determined by flame spectrophotometry. The transfer, amalgamation, and dilution of the three samples took approximately 3 hours.

RESULTS OF ANALYSIS OF FIRST ROUND-

ROBIN SAMPLES OF POTASSIUM

SUBMITTED TO ORNL

Section	Sample weight, g	Oxygen, ppm
Sample B-16		
Top	1.41	22
Middle	1.49	26
Bottom	1.45	24
Sample B-20		
Top	1.43	21
Middle	1.54	19
Bottom	1.47	22

REFERENCE

1. Goldberg, Gerald: Determination of Oxygen in Higher Alkali Metals. ORNL-3397, Anal. Chem. Div. Annual Prog. Rept. ending Dec. 31, 1962, Oak Ridge Nat. Lab., 1963, pp. 50-52.

UNITED NUCLEAR CORPORATION

APPARATUS

The apparatus consists of an amalgamation tube assembly, a high-vacuum system, and a mercury reservoir. The amalgamation tube assembly is composed of a reaction tube for the amalgamation and extraction of samples, a receiver for draining mercury, and interconnecting tubing and stopcocks. The amalgamation tube is connected to the high-vacuum system, the mercury reservoir, and the receiver through a short Y-connection equipped with two stopcocks and spherical O-ring type joints. This construction permits the amalgamation tube to be disassembled and placed in a dry box for loading of a sample after cutting.

Titrations are performed with a Beckman Zeromatic pH meter and a micrometer-type burette, 2-milliliter capacity.

REAGENTS

(1) Mercury - triple distilled, cp grade
(2) Argon - 99.998 percent purity
(3) Hydrochloric acid - 0.01 N solution
(4) Sulfuric acid - 4.5 N solution
(5) Sodium hydroxide - 1 N solution

PREPARATION OF SAMPLES

The sample tube and the clean, dry amalgamation tube are placed in a glove-type dry box, arranged to permit operation in an atmosphere of purified argon. A 1/2-inch sample is cut from the bottom end of the sample tube and discarded. A sample $1\frac{1}{4}$ inches long is then cut and placed in the amalgamation tube; the amalgamation tube is then reassembled, removed from the dry box, and connected to the high-vacuum system.

The atmosphere of the dry box is monitored by a UNC gas purity tester. All tools and instruments are carefully cleaned and degreased before use. The remainder of the sample tube is stored in the dry box until needed.

ANALYTICAL PROCEDURE

The sample is amalgamated by adding mercury to the evacuated amalgamation tube and heating. After cooling, the excess mercury and amalgam are drained into the reservoir, making sure that all the residue is retained in the tube. Mercury is again added to the tube and drained into the reservoir after 5 minutes. Extractions are continued until a test of the residue indicates complete removal of the potassium amalgam. A magnet is used to stir the mercury and wash down the walls of the tube during the extractions. Normally five to six extractions are required.

When extraction is complete, the excess mercury remaining in the tube is drained into a beaker. The tube is rinsed thoroughly with distilled water and the washings added to the beaker. The solution is then titrated with 0.01 N hydrochloric acid added from a 2-milliliter capacity micrometer burette to an end point of 5.8 as measured by a Beckman Zeromatic pH meter. Purified argon gas is bubbled through the solution during the titration.

The sample size is determined by acidifying the combined mercury extracts with 4.5 N sulfuric acid and back titrating with 1 N sodium hydroxide solution.

Calculations are made assuming that the residue contains oxygen combined as K_2O. The following results were obtained:

Sample tube	Sample	Oxygen content, ppm
B-5	1	46
	2	50
	4	36
B-6	1	49
	3	40
	4	66
B-17	1	183
	2	40
	3	40
	4	32

The high value for sample 1 from tube B-17 resulted from a poor atmosphere, which developed in the dry box during cutting of the sample. Sample 3 from tube B-5 and sample 2 from tube B-2 were lost because of cracking of the reactor tube during amalgamation.

Each sample consisted of a $1\frac{1}{4}$-inch length of the specimen tube containing 1.2 to 1.3 grams of potassium. Samples were numbered consecutively, starting at the bottom end of the tube. Approximately 1/2 inch at the end of each tube was discarded.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LEWIS RESEARCH CENTER

Liquid Metals Branch

by W. A. Dupraw, J. W. Graab, and R. Gahn

Much interest has been evinced recently in the use of potassium as a thermodynamic working fluid in space nuclear turboelectric power systems. Since oxygen impurities in alkali metals (even below 20 ppm in some cases) have been recognized as promoting and accelerating corrosion attack on containment materials, it is important that a reliable method for determining the oxygen content of potassium be available.

Currently the technique most widely used for the measurement of oxygen in potassium is the Pepkowitz-Judd amalgamation technique (ref. 1). It is our belief that a major source of error in this technique is the inadvertent introduction of oxygen or water contamination during the processes of sampling, transfer, and analysis. This contamination should not be unexpected in view of the reactivity of potassium with oxygen and water and the questionable handling techniques currently employed. It then follows, if this contention is correct, that extreme care must be exercised in the handling and analytical procedures. Preferably, all steps should be carried out in a high-vacuum environment with a continuous monitoring of the pressure by means of a high-vacuum gage.

In an attempt to improve the analytical precision of the Pepkowitz-Judd technique for determining oxygen in potassium, the following innovations were made:

(1) The entire system complex - sample tube, transfer section, and amalgamation system - was maintained under a high vacuum.

(2) The amalgamation reaction system volume was made small.

(3) A ball check valve was used to contain the vigorous amalgamation reaction.

(4) Flanged O-ring joints were used to eliminate greased or waxed joints.

(5) Replicate samples were taken from a single sample tube.

The apparatus consisted of two major components: a metal extruder and a glass extraction system. The glass and metal components were connected by O-ring joints, and the entire apparatus was evacuated to a pressure between 2×10^{-5} and 4×10^{-6} torr.

The sample container was a stainless-steel tube $6\frac{3}{4}$- by $\frac{5}{16}$-inch inside diameter. It was vacuum filled with liquid metal, capped, and stored under vacuum until used. For analyses, the sample tube was mounted in the extruder section apparatus.

After the apparatus had attained operational vacuum, a small portion of the potassium was extruded from the sample tube, cut with a hot wire, and discarded in the waste tray. The analytical sample was then extruded, cut off, and dropped into the glass extraction system. The extruder was sealed from the extraction system with a valve and the ball check valve was seated in place to confine the amalgamating reaction. Triple distilled mercury was then admitted to the extraction system. After the reaction had occurred, manipulation of a glass-covered magnetic bar within the extraction system removed all film from the chamber walls. By means of a valve on the restricted end of the extraction system, the amalgam was slowly removed into the receiving flask. The exit valve was closed, approximately 15 milliliters of mercury was admitted to the extraction system, and the magnetic bar manipulation was repeated. The wash mercury was removed as before. A total of five similar washes was made to remove completely the potassium amalgam; approximately 700 to 900 grams of mercury was used in all.

The glass extraction portion of the system was brought to atmospheric pressure and the extraction system and amalgam receiving flask removed. Up to this point, the total time for the operation was approximately 1 hour.

The potassium was extracted from the amalgam with boiled distilled water and titrated with standard acid to determine the weight of alkali sample used.

The potassium oxide was washed out of the extraction chamber with boiled distilled water and titrated with standard 0.005 N acid using a microburette. Methyl red was used as an indicator in both titrations.

REFERENCE

1. Pepkowitz, Leonard P.; and Judd, William C.: Determination of Sodium Monoxide in Sodium. Anal. Chem., vol. 22, no. 10, Oct. 1950, pp. 1283-1286.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LEWIS RESEARCH CENTER

Chemical Services Unit

by David E. Kuivinen

METHOD

The mercury amalgamation method is predicated on the solubility of sodium in mercury and the insolubility of sodium oxide. The alkali oxide floats on the surface of the mercury and can be effectively separated by repeated additions of mercury. The total alkali content is determined by reacting the alkali metal amalgam with an excess of standard acid and back titration of the excess with standard hydroxide solution. The oxide fraction is reacted with distilled water and titrated with dilute standard acid for the oxide content.

The Pratt & Whitney development of the amalgamation procedure requires the use of a vacuum dry box for environmental control with an inert gas atmosphere. Control and monitoring of the oxygen content in the inert cover gas enable the determination of low orders of oxygen concentration.

APPARATUS

The following test equipment was used:

Inert atmosphere vacuum dry box. - A stainless-steel vacuum dry box equipped with a 15-cubic-foot-per-minute vacuum pump, molecular sieve dryer beds, an evacuable air lock, and polyvinyl chloride dry box gloves was used for the test unit.

Trace oxygen analyzer. - The trace oxygen analyzer was designed to measure traces of oxygen (0 to 100 ppm) in other gases. It had a high range (0 to 100 ppm) and a low range (0 to 10 ppm) with a ±5 percent full-scale accuracy. The basic oxygen measuring element was a galvanic cell consisting of a silver cathode and an anode made of active cadmium; the electrode was separated by a porous tube saturated with potassium hydroxide. Oxygen in the sample gas is adsorbed on the surface of the cathode and goes into solution in the electrolyte as hydroxyl ions. The cadmium anode is oxidized to cad-

mium hydroxide and causes a current to flow in an external circuit. The millivolt output of the cell is directly proportional to the oxygen concentration in the sample gas.

Separatory funnels. - The separatory funnels were 250-milliliter Pyrex funnels equipped with Teflon stopcocks.

Refrigeration unit for NaK, cesium, and rubidium. - Sodium-potassium alloys (NaK), cesium, and rubidium require special handling techniques because of their low melting points and their being liquid or near liquid at ambient temperatures. In order to utilize the amalgamation procedure, the activity of the metal must be reduced to a safe handling rate by freezing the metal and handling it as a solid such as sodium. A 1- by 6- by 12-inch stainless-steel rectangular refrigeration plate was placed into the dry box with a 6- by 6- by 12-inch Plexiglas box for insulation. Acetone, cooled externally with a dry-ice - acetone mixture, was used as the circulating refrigerant and cooled to -50° C in order to freeze a sample of NaK in Pyrex. The sample was frozen within 15 minutes, cut with a triangular file, broken, and amalgamated with mercury in the usual way.

Tubing cutters will be mounted internally on a wall of the Plexiglas box in order to cut samples contained in metal tubing. The use of cutters would prevent the possible melting of the sample when it is handled by warm gloved hands.

REAGENTS (MATERIALS)

The following reagents and materials were used:

(1) Standard solutions:

    Sulfuric acid, 0.5 N

    Sulfuric acid, 0.002 N

    Sodium hydroxide, 0.5 N

(2) Mercury, triple distilled

(3) Argon gas, dry-prepurified, 99.997 percent argon

PROCEDURES

The dry box was evacuated to a pressure of about 25 microns, back filled with dry, oxygen-free argon, and pressurized to 1 pound per square inch gage. The oxygen content of the argon cover gas in the dry box was tested with the trace oxygen analyzer. If the oxygen content was greater than 1 ppm, the purge was repeated until a value of 1 ppm was obtained.

Approximately 20 milliliters of tripled distilled mercury was added to a 250-milliliter Pyrex separatory funnel with a Teflon stopcock. A sodium sample of about 0.5 to 1.0 gram was center cut from the sample tube and added to the mercury in the amalgamation chamber. Sample tubes of glass may be cut with a triangular file and those in metal tubes with tubing cutters. Sections of sample tubes cut from 0.5 to 1 inch will usually provide a large enough sample.

The sample was shaken for 3 minutes, held for 30 seconds, and all but 3 milliliters of the amalgam was drawn off into a marked bottle. The additions and separations were repeated six times with 15 milliliters of mercury. In the last extraction, a small portion of the amalgam was poured into a separate beaker and checked for completeness of extraction by adding water and phenolphthalein to the beaker outside the box. When no color was present, the extraction was considered complete and all the material was removed from the box.

The sodium oxide extract remaining in the separatory funnel was dissolved in 50 milliliters of distilled water and titrated with 0.002 N sulfuric acid to a pH of 7 by means of a titrimeter.

The alkali metal - mercury amalgam was reacted with an excess volume of 0.5 N sulfuric acid. The excess acid was back titrated with 0.5 N sodium hydroxide to a pH of 7.

CALCULATIONS

(1) Sample weight:

$$W = (N_a V_a - N_b V_b) \text{ (meq wt of alkali metal)}$$

where

W	sample weight, g
N_a	normality of the 0.5 N sulfuric acid used to extract alkali metal from amalgam
V_a	volume of 0.5 N sulfuric acid used, ml
N_b	normality of 0.5 N sodium hydroxide
V_b	volume of 0.5 N sodium hydroxide used to titrate excess 0.5 N sulfuric acid

Milliequivalent weights: sodium, 0.023; potassium, 0.039; NaK, 0.028; cesium, 0.133; rubidium, 0.085

(2) Oxygen content:

$$\frac{N_a V_a 0.008 \times 10^6}{W}$$

where

N_a	normality of 0.002 N sulfuric acid used to titrate oxide
V_a	volume of 0.002 N sulfuric acid used, ml
0.008	milliequivalent weight of oxygen
W	weight of sample, g

Attendees at NASA Round-Robin Meeting

June 4, 1964

Mr. Charles A. Barrett, NASA Lewis Research Center

Mr. Robert Cleary, Pratt & Whitney Aircraft, CANEL

Mr. George Cobel, Dow Chemical Company

Mr. L. E. Dotson, General Electric Company

Mr. William A. Dupraw, NASA Lewis Research Center

Mr. Randall Gahn, NASA Lewis Research Center

Mr. Gerald Goldberg, Oak Ridge National Laboratory

Mr. Judson W. Graab, NASA Lewis Research Center

Mr. C. C. Gregg, United Nuclear Corporation, Development Division

Dr. Robert Hand, General Electric Company

Mr. E. W. Hobart, Pratt & Whitney Aircraft, CANEL

Dr. Kramer, Dow Chemical Company

Mr. Thomas Lejac, General Electric Company

Mr. Russell Lindberg, NASA Lewis Research Center

Mr. A. P. Litman, Oak Ridge National Laboratory

Dr. Wilson Mausteller, MSA Research Corporation

Mr. Sheridan Rodgers, MSA Research Corporation

Dr. Louis Rosenblum, NASA Lewis Research Center

Mr. James W. Slough, NASA Lewis Research Center

Dr. James H. Swisher, NASA Lewis Research Center

Mr. Glenn R. Zellars, NASA Lewis Research Center